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Radionuclide Concentrations in Bivalves Collected Along the Coastal United States

NATHALIE J. VALETTE-SILVER and GUNNAR G. LAUENSTEIN
National Status and Trends Program, N/ORCA 21, National Oceanic & Atmospheric Administration, 1305 East–West Highway, Silver Spring, MD 20910, USA

In 1990, the National Oceanic and Atmospheric Administation's National Status and Trends Program initiated a study of artificial radionuclides (^{241}Am, $^{239+240}$Pu, ^{238}Pu, ^{137}Cs, ^{110}Ag, ^{90}Sr, ^{65}Zn, ^{60}Co, and ^{58}Co) in oysters and mussels collected along the coastal US. The results of this study show that activation products ^{110}Ag, ^{65}Zn, ^{60}Co and ^{58}Co are sometimes present close to nuclear facilities. In addition, based on a nonparametric Kruskal–Wallis statistical test, it appears that ^{241}Am and ^{137}Cs concentrations as well as ^{241}Am/$^{239+240}$Pu and ^{137}Cs/^{40}K activity ratios are highest along the West Coast of the US. For ^{238}Pu, $^{239+240}$Pu, and ^{90}Sr activities and the other ratios, the differences observed in the distribution of the radionuclides between the various coasts are not statistically significant. There is also a statistical difference between the values of the $^{239+240}$Pu/^{90}Sr ratio in oysters vs mussels collected along the East Coast and of the ^{241}Am/$^{239+240}$Pu ratio between two species of mussels collected along the West Coast. Finally, when the NOAA results for ^{241}Am, $^{239+240}$Pu, and ^{137}Cs are compared with those of an earlier (1976–1978) Mussel Watch Program sponsored by the Environmental Protection Agency, the statistical Sign Test generally shows a significant decrease in the concentrations between the mid-1970s and the early 1990s.

The National Oceanic and Atmospheric Administration's (NOAA's) National Status and Trends Program (NS&T) was initiated in 1984 to monitor the environmental quality of US coastal and estuarine areas. The programme includes two main monitoring projects: the National Benthic Surveillance Project, initiated in 1984, which collects and analyses sediments and bottom fish from 149 sites; and the Mussel Watch Project (MWP), initiated in 1986, which collects and analyses bivalves (mussels and oysters) and sediments from over 250 sites. Until 1990, each site was sampled and collected material analysed on a yearly basis for 14 elements (major and trace elements) and 70 organic contaminants (polyaromatic hydrocarbons, polychlorinated biphenyl congeners, pesticides, and butyltins).

Because bivalves concentrate contaminants while filtering surrounding waters, these organisms are useful indicators of changes occurring in the chemistry of their environment. While their response to chemical changes in their surroundings may be detectable within a matter of days, depending on the species and on the contaminant, approximately 4–24 weeks are required for the bivalves to equilibrate with their environment (Roesijadi *et al.*, 1984; Sericano, 1993).

In 1990, bivalves were collected at 36 sites (Fig. 1) and analysed for the radionuclides: ^{241}Am, $^{239+240}$Pu, ^{238}Pu, ^{137}Cs, ^{110}Ag, ^{90}Sr, ^{65}Zn, ^{60}Co, ^{58}Co, ^{40}K, and ^{7}Be. Most of these 36 samples were obtained from MWP sites and the remaining samples were collected in the vicinity of nuclear facilities or known radioactive dumping sites. Three mollusc species were collected for this project: *Mytilus edulis* species complex along the North Atlantic and Pacific coasts; *Mytilus californianus*, generally found in high-energy environments on the Pacific Coast; and *Crassostrea virginica*, collected along the Atlantic shore from Delaware Bay to Florida and along the Gulf of Mexico coast (Table 1).

Between 1976 and 1978, the Environmental Protection Agency (EPA) conducted a Mussel Watch Program (MWP70s) that measured transuranic elements, polyaromatic hydrocarbons, polychlorinated biphenyls, chlorinated pesticides, and trace metals in bivalves collected around the country (Farrington, 1983; Farrington *et al.*, 1983; Goldberg *et al.*, 1978, 1983; Palmieri *et al.*, 1984). Thirty of the 36 sites sampled in 1990 are close to sites sampled in the 1970s. It is then possible to compare the results from the two sampling times for those sites. Comparisons were possible for the four radionuclides measured by both programmes (i.e. ^{241}Am, $^{239+240}$Pu, ^{238}Pu, and ^{137}Cs).

The first test of a nuclear weapon occurred in July 1945 at Alamogordo (NM, USA). Following the atomic bombings of Nagasaki and Hiroshima in August of 1945, several US nuclear devices were detonated on islands of the Pacific Ocean and at the Nevada Test Site

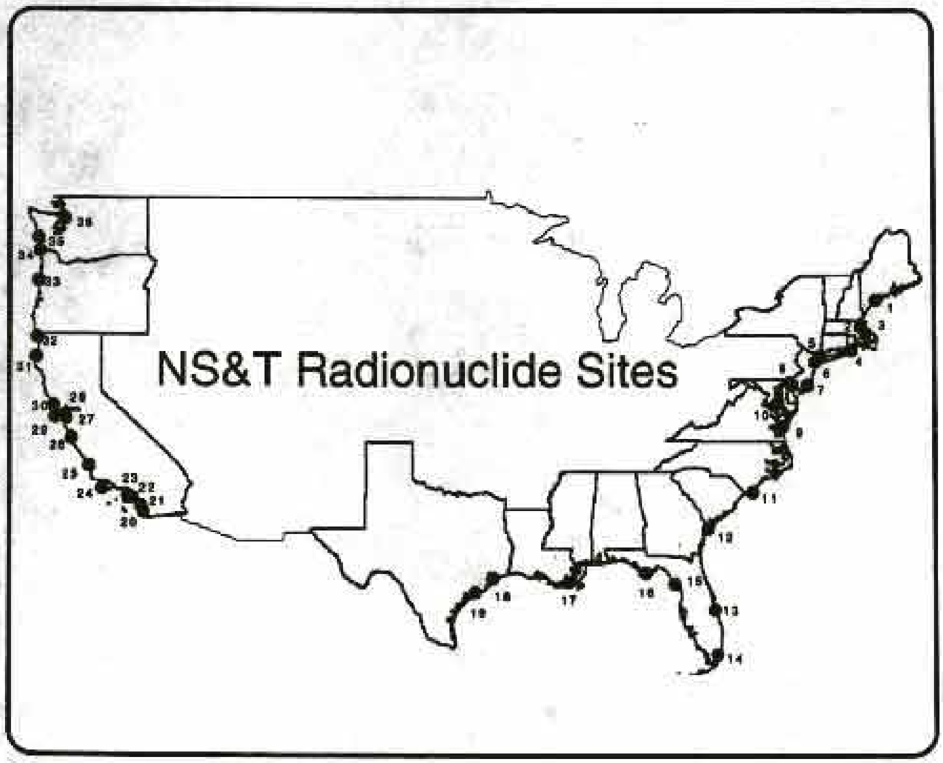

Fig. 1 Map showing the location of the NS&T sites where bivalves were collected for the NOAA NS&T Radionuclide Project.

TABLE 1
Location of the NS&T sites.

Site no.	Main location, specific location (acronym)	State	Species
East Coast			
1*	Merriconeag Sound, Stover Point (MSSP)	ME	*Mytilus edulis*
2*	Boston Harbor, Deer Island (BHDI)	MA	*Mytilus edulis*
3*	Duxbury Bay, Clarks Island (DBCI)	MA	*Mytilus edulis*
4*	Block Island Sound, Block Island (BIBI)	RI	*Mytilus edulis*
5*	Long Island Sound, Hempstead Harbor (LIHH)	NY	*Mytilus edulis*
6*	Hudson/Raritan Estuary, Jamaica Bay (HRJB)	NY	*Mytilus edulis*
7*	Absecon Inlet, Atlantic City (AIAC)	NJ	*Mytilus edulis*
9	Delaware Bay, Arnolds Point Shoal (DBAP)	DE	*Crassostrea virginica*
8*	Chesapeake Bay, Cape Charles (CBCC)	VA	*Crassostrea virginica*
10	Chesapeake Bay, Calvert Cliff (CBCL)	MD	*Crassostrea virginica*
11*	Cape Fear, Battery Island (CFBI)	NC	*Crassostrea virginica*
12*	Savannah River Estuary, Tybee Island (SRTI)	GA	*Crassostrea virginica*
13	Indian River, Sebastian River (IRSR)	FL	*Crassostrea virginica*
14	Biscayne Bay, Gould's Canal (BBGC)	FL	*Crassostrea virginica*
Gulf			
15*	Cedar Key, Black Point (CKBP)	FL	*Crassostrea virginica*
16*	Apalachicola Bay, Cat Point Bar (APCP)	FL	*Crassostrea virginica*
17*	Barataria Bay, Middle Bank (BBMB)	LA	*Crassostrea virginica*
18*	Galveston Bay, Hanna Reef (GBHR)	TX	*Crassostrea virginica*
19*	Matagorda Bay, East Matagorda (MBEM)	TX	*Crassostrea virginica*
West Coast			
20*	Oceanside, Municipal Beach Jetty (OSBJ)	CA	*Mytilus edulis*
21*	La Jolla, Point La Jolla (LJLJ)	CA	*Mytilus californianus*
22	Newport Beach, West Jetty (NBWJ)	CA	*Mytilus californianus*
23*	San Pedro Harbor, Fishing Pier (SPFP)	CA	*Mytilus edulis*
24	Santa Cruz Island, Fraser Point (SCFP)	CA	*Mytilus californianus*
25*	San Luis Obispo Bay, Point San Luis (SLSL)	CA	*Mytilus californianus*
26*	Pacific Grove, Lovers Point (PGLP)	CA	*Mytilus californianus*
27*	San Francisco Bay, San Mateo Bridge (SFSM)	CA	*Mytilus edulis*
28*	San Francisco Bay, Emeryville (SFEM)	CA	*Mytilus edulis*
29*	Farallon Islands, East Landing (FIEL)	CA	*Mytilus californianus*
30*	Bodega Bay, Bodega Bay Entrance (BBBE)	CA	*Mytilus californianus*
31*	Humboldt Bay, Beach Jetty (HMBJ)	CA	*Mytilus californianus*
32*	Crescent City, Point St. George (SGSG)	CA	*Mytilus californianus*
33*	Yaquina Bay, Yaquina Head (YHYH)	OR	*Mytilus californianus*
34*	Columbia River, South Jetty (CRSJ)	OR	*Mytilus edulis*
35*	Grays Harbor, Westport Jetty (GHWJ)	WA	*Mytilus californianus*
36*	Whidbey Island, Possession Point (WIPP)	WA	*Mytilus edulis*

*Common sites to NOAA NS&T and to EPA Mussel Watch Project (MWP70s).

(Carter & Moghissi, 1977). In the early 1950s, there was an active period of atmospheric weapons testing by the USA, UK, and the former USSR. A moratorium on nuclear testing was initiated in November 1958 and ended in September 1961. The pre-moratorium period was dominated by US weapons testing and the post-moratorium period was dominated by the former USSR weapons testing. From 1966 to 1974, most of the atmospheric tests were conducted by France in the Tuamotu Archipelago (Mururoa and Fantataufa Islands) and by the People's Republic of China (Koide *et al.*, 1979, 1985). In 1974, France joined the USA and USSR in conducting only underground tests and, in 1980, the People's Republic of China is believed to have followed suit. India detonated its first weapon underground in 1974. Presently, all known nuclear testing is underground, including the large events recorded in May 1992 and October 1993 from the People's Republic of China (Davis, pers. comm.).

The phase of intense atmospheric nuclear testing resulted in the injection into the upper atmosphere of a broad array of fission and fusion products as well as induced radionuclides and in a global fallout of radionuclides. The longer lived radionuclides ($T_{1/2} > 2$ years) from this source still persist in the environment.

In 1964, there was an additional input of ^{238}Pu to the atmosphere due to the burn-up of the plutonium-fueled SNAP-9A satellite (Mamuro & Matsunami, 1969; Koide *et al.*, 1977).

The occurrence of the fission product radionuclides ^{241}Pu ($T_{1/2}$=14.9 years), ^{241}Am ($T_{1/2}$=458 years), ^{239}Pu ($T_{1/2}$=24 400 years), ^{240}Pu ($T_{1/2}$=6580 years), ^{238}Pu ($T_{1/2}$=86 years), ^{137}Cs ($T_{1/2}$=30 years), and ^{90}Sr ($T_{1/2}$=28 years) in the environment is mostly derived from global fallout associated with this intense period of atmospheric testing, including redistribution from remobilized soil particles (Noshkin & Bowen, 1973; Olsen *et al.*, 1981a,b; Bopp *et al.*, 1982). Nuclear reactor accidents, such as Chelyabinsk (September 1957) and Chernobyl (April 1986) in the former USSR, have also released fission products such as ^{137}Cs into the atmosphere. However, because these inputs were released into the lower atmosphere, their distribution appears to be localized (i.e. a distance of hundreds of km, Mélière *et al.*, 1988; Pyatt & Beaumont, 1992).

Some shorter lived artificial radionuclides, such as ^{110}Ag ($T_{1/2}$=253 days), ^{65}Zn ($T_{1/2}$=243.6 days), ^{60}Co ($T_{1/2}$=5.3 years), and ^{58}Co ($T_{1/2}$=71.3 days), are formed by activation in nuclear reactors and can be released to the environment with nuclear power plant cooling waters.

^{40}K ($T_{1/2}=1.28\times10^{9}$ years) occurs naturally in the environment, and ^{7}Be ($T_{1/2}$=53.4 days) is formed in the upper atmosphere by cosmic ray bombardment of oxygen and nitrogen nuclei. The results obtained for both the ^{40}K and ^{7}Be analyses are mostly used here as reference.

The aim of this study is to determine the present status of radionuclide contamination in the coastal and estuarine environments of the US and to document the changes that have occurred in this contamination over the last 15 years.

Methods and Results

As for all the other contaminants analysed by the NS&T programme, each of the 36 samples used to analyse the radionuclides was a composite of molluscs collected at three stations within a site. Consequently, the results account for the site variability. The precision reported for each analysis is based on counting errors (Table 2).

In order to obtain about 300 g of dry soft tissue, approximately 180–200 mussels, or at least 125–150 oysters, were used for each site. Unfortunately, in a few cases, due to the small size of the molluscs and their high moisture content, < 100 g of dried sample was recovered, leading to high analytical uncertainties. After collection, the animals were packed in plastic containers and frozen on dry ice until shucked for analysis. The samples were shipped overnight to Texas A&M University, Geochemical and Environmental Research Group (GERG) where they were thawed and shucked and the soft tissues were freeze-dried and weighed. The dried samples were then shipped in sealed glass containers to Thermo Analytical Inc., California Laboratories (TMA/Norcal). At TMA/Norcal, the samples were redried, reweighed, charred, and ashed at 425°C. After appropriate radiochemical separation, the samples were analysed for the various isotopes using α, β, and γ counting techniques (see the Appendix for analytical details).

Table 2 displays the data obtained for the NOAA NS&T study. All the results are expressed in Bq g^{-1} (1 Ci=3.7×10^{10} Bq) of material (dry weight). Along the US coasts fallout radioisotope concentrations range from 0.47×10^{-6} to $\sim90\times10^{-6}$ Bq g^{-1} for ^{241}Am (Fig. 2), from 1.21×10^{-6} to 88.4×10^{-6} Bq g^{-1} for $^{239+240}$Pu, from 1.26×10^{-6} to 59.2×10^{-6} Bq g^{-1} for ^{238}Pu, from 17×10^{-6} to 400×10^{-6} Bq g^{-1} for ^{137}Cs, and from $\sim16\times10^{-6}$ to 1994×10^{-6} Bq g^{-1} for ^{90}Sr.

The activation products are generally below detection limits (Table 2), with the following exceptions: ^{110}Ag=1.2×10^{-2} Bq g^{-1} ($\pm$15%) at Chesapeake Bay–Calvert Cliff, ^{65}Zn=3.7×10^{-2} Bq g^{-1} ($\pm$37%) at Delaware Bay–Arnolds Point Shoal and ^{65}Zn=0.37×10^{-2} Bq g^{-1} ($\pm$75%) at La Jolla–Point La Jolla, ^{60}Co=0.10×10^{-2} Bq g^{-1} ($\pm$90%) at Santa Cruz–Fraser Point, and ^{58}Co=0.93×10^{-2} Bq g^{-1} ($\pm$12%) at Savannah River–Tybee Island.

Finally, concentrations of naturally occurring ^{40}K range from 0.4 to 46×10^{-2} Bq g^{-1}, and ^{7}Be was only detected at one site in the Pacific Northwest (site SGSG=1.5×10^{-2} Bq g^{-1} $\pm$98%).

Interpretation

Geographical distribution of radioactivity in the coastal USA

For each radioisotope, geometric average and median activities were calculated for the whole set of data (Total) and by coast (East, Gulf, West). Results of geometric means were generally very close to the median values that are reported in Table 3.

TABLE 2
Isotope activities (Bq g^{-1}) and ratios

	Isotope activities												Isotope ratios*						
NS&T	^{40}K $\times 10^{-2}$	K ± %	^{90}Sr $\times 10^{-4}$	Sr ± %	^{137}Cs¶ $\times 10^{-4}$	Cs ± %	^{238}Pu $\times 10^{-4}$	Pu ± %	$^{239+240}Pu$ $\times 10^{-4}$	Pu ± %	^{241}Am $\times 10^{-4}$	Am ± %	Cs/Sr	Cs/K $\times 10^{-3}$	Sr/K $\times 10^{-4}$	$^{238}Pu/Pu^*$	Pu*/Cs	Pu*/Sr	Am/Pu*
MSSP	0.27	10	56.2	776	<†	–‡	4.88	200	47.0	42	6.25	229	–	–	2.05	0.10	–	0.84	0.13
BHDI	0.35	10	27.0	932	192	150	1.84	300	11.9	77	1.14	900	7.11	0.55	0.77	0.15	0.06	0.44	0.10
DBCI	0.28	8	27.0	810	195	128	1.58	200	27.4	32	7.92	61	7.23	0.71	0.98	0.06	0.14	1.02	0.29
BIBI	0.33	10	25.7	910	<	–	2.65	200	14.5	55	6.77	300	–	–	0.77	0.18	–	0.56	0.47
LIHH	0.23	8	31.5	140	103	158	1.26	267	1.25	267	1.27	200	3.27	0.44	1.36	1.01	0.01	0.04	1.01
HRJB	0.29	26	181	180	<	–	20.1	200	12.0	267	8.66	267	–	–	6.34	1.68	–	0.07	0.72
AIAC	0.32	50	503	150	<	–	<	–	46.3	267	8.33	600	–	–	15.96	–	–	0.09	0.18
DBAP	0.34	15	124	240	<	–	4.92	300	2.45	800	<	–	–	–	3.61	2.01	–	0.02	–
CBCC	0.40	10	16.5	1600	<	–	3.92	150	1.95	300	8.10	100	–	–	0.41	2.02	–	0.12	4.16
CBCL	0.28	9	209	45	74.0	320	5.22	89	7.55	77	0.47	600	0.35	0.26	7.44	0.69	0.10	0.04	0.06
CFBI	0.33	14	733	80	<	–	2.38	600	28.5	67	7.40	267	–	–	22.05	0.08	–	0.04	0.26
SRTI	0.40	12	117	246	<	–	13.2	200	4.37	600	NA§	–	–	–	2.9	3.02	–	0.04	–
IRSR	0.29	10	37.4	631	<	–	5.33	160	10.6	100	6.88	114	–	–	1.29	0.50	–	0.28	0.65
BBGC	0.04	10	692	174	<	–	16.3	150	4.07	600	5.03	400	–	–	155.8	4.01	–	0.01	1.24
CKBP	0.39	21	98.4	150	<	–	59.2	134	88.4	90	10.7	300	–	–	2.51	0.67	–	0.90	0.12
APCP	0.46	11	46.3	237	<	–	4.66	250	18.5	63	0.95	1000	–	–	1.01	0.25	–	0.40	0.05
BBMB	0.25	13	34.0	265	17.0	2100	4.96	115	4.22	1324	NA	–	0.50	0.07	1.34	1.18	0.25	0.12	–
GBHR	0.24	9	71.4	169	82.9	510	1.77	160	2.83	100	1.25	400	1.16	0.35	3.03	0.63	0.03	0.04	0.44
MBEM	0.32	10	377	76	91.8	390	1.40	300	7.70	91	31.6	51	0.24	0.29	11.78	0.18	0.08	0.02	4.11
OSBJ	0.29	9	27.0	161	400	130	2.74	200	8.21	90	11.8	172	14.79	1.37	0.93	0.33	0.02	0.30	1.44
LJLJ	0.27	11	30.5	380	360	100	1.86	200	4.66	81	69.9	29	11.81	1.31	1.11	0.40	0.01	0.15	15.00
NBWJ	0.24	11	61.4	120	295	146	2.74	150	2.05	267	6.51	175	4.80	1.25	2.6	1.33	0.01	0.03	3.17
SPFP	0.29	16	49.6	730	<	–	2.42	300	1.21	600	4.88	500	–	–	1.72	2.00	–	0.02	9.79
SCFP	0.27	9	68.8	304	189	200	1.56	300	27.2	35	86.6	20	2.75	0.71	2.59	0.06	0.14	0.40	3.18
SLSL	0.31	9	23.2	276	112	136	<	–	10.9	34	19.4	35	4.86	0.37	0.75	0.00	0.10	0.47	1.78
PGLP	0.29	13	50.7	270	<	–	<	–	6.44	300	67.7	31	–	–	1.73	0.00	–	0.13	10.52
SFSM	0.22	10	27.3	138	322	70	3.35	111	7.07	53	2.01	150	11.78	1.43	1.22	0.47	0.02	0.26	0.28
SFEM	0.29	17	45.1	462	<	–	1.34	1000	15.9	84	23.9	81	–	–	1.55	0.08	–	0.35	1.50
FIEL	0.31	9	50.7	81	118	200	2.31	160	18.4	36	64.8	23	2.32	0.38	1.63	0.13	0.16	0.36	3.52
BBBE	0.26	9	32.3	402	177	96	1.89	115	17.0	26	53.3	24	5.47	0.68	1.24	0.11	0.10	0.53	3.14
HMBJ	0.20	10	45.1	110	313	74	11.9	74	15.1	73	44.8	42	6.94	1.53	2.21	0.79	0.05	0.33	2.97
SGSG	0.38	9	1994	88	122	288	1.64	500	20.5	49	89.9	19	0.06	0.32	52.84	0.08	0.17	0.01	4.39
YHYH	0.25	10	172	54	<	–	NA	–	NA	–	49.6	27	–	–	6.94	–	–	–	–
CRSJ	0.32	9	144	139	268	216	2.86	300	24.2	60	12.7	63	1.86	0.83	4.44	0.12	0.09	0.17	0.53
GHWJ	0.31	11	27.5	632	280	144	2.29	200	9.18	100	7.29	172	10.16	0.90	0.88	0.25	0.03	0.33	0.79
WIPP	0.24	12	76.2	510	<	–	8.58	120	10.3	100	4.85	200	–	–	3.22	0.83	–	0.13	0.47

Pu; The sum of ^{239}Pu and ^{240}Pu unless otherwise noted.
† <; Data that are below the detection limit.
‡ –; Precision could not be calculated because the result was below the detection limit.
§ NA; Samples not analysed for these radionuclides.
¶ All results reported here were obtained after chemical separation and β counting, a method that achieves lower detection limits than those obtained by direct α counting.

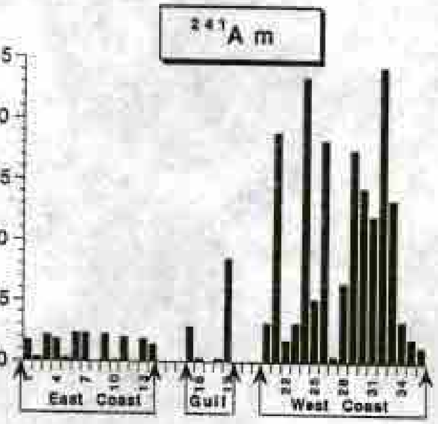

Fig. 2 Bar chart showing the activity of ^{241}Am in Bq $g^{-1} \times 10^{-6}$ (on the vertical axis) displayed as a function of site location (horizontal axis) given in a geographical order from the north of the East Coast through the Gulf of Mexico and ending in the Pacific Northwest. The correspondence between site numbers, site names and acronyms is given in Table 1.

As expected for a naturally occurring radionuclide, ^{40}K concentrations show small spatial variation.

For the activation products and ^{7}Be, averages and medians were not calculated because only a few of the data points were above the detection limits. In most cases, several months elapsed between collection time and analysis of the samples, explaining why ^{7}Be ($T_{1/2}$ = 53.4 days) and other relatively short-lived radionuclides were rarely measured in our samples. With the exception of Fraser Point, all the detectable spikes of short-lived activation products (Table 2) appear at sites located close to known nuclear facilities.

For ^{241}Am, the medians are comparable for samples collected on both East and Gulf Coasts (7×10^{-6} and 6×10^{-6} Bq g^{-1}, respectively), but different from the medians found in bivalves collected along the West Coast (24×10^{-6} Bq g^{-1}). Using the nonparametric Kruskal–Wallis test, it appears that the difference between activities of samples collected on the West Coast and on the other coasts of the US is significant ($p < 0.05$). Along the Pacific Coast, the activities of this radionuclide (Fig. 2) display a clear geographic pattern, with the maximal activity being measured in Northern California near Point Saint George (CA). In addition to this general pattern, isolated high values are present in other locations along the Californian Coast near Point La Jolla ($\sim 70 \times 10^{-6}$ Bq g^{-1}), Santa Cruz Island ($\sim 87 \times 10^{-6}$ Bq g^{-1}), Monterey Bay ($\sim 68 \times 10^{-6}$ Bq g^{-1}), and the Farallon Islands ($\sim 65 \times 10^{-6}$ Bq g^{-1}). Activities are fairly variable along the Gulf Coast where two sites, located near Cedar Key (FL) and Matagorda Bay (TX), show concentrations as high as ~ 11 and $\sim 32 \times 10^{-6}$ Bq g^{-1}, respectively. Along the East coast, values are almost uniformly low.

The median of the concentrations reported for $^{239+240}$Pu (Tables 2 and 3) is lower for the Gulf ($\sim 8 \times 10^{-6}$ Bq g^{-1}) than for the other coasts ($\sim 11 \times 10^{-6}$ Bq g^{-1}). However the Kruskal–Wallis test shows that the difference is not statistically significant at the 5% level. Along the Gulf of Mexico, the oysters collected near Cedar Key (FL) display the highest activity ($\sim 88 \times 10^{-6}$ Bq g^{-1}) measured in our data set, explaining why the average value is so high compared to the median value. Along the East Coast, several high values are also observed (Stover Point in Maine, 47×10^{-6} Bq g^{-1}; Duxbury Bay in Massachusetts, $\sim 27 \times 10^{-6}$ Bq g^{-1}; Absecon Inlet in New Jersey, $\sim 46 \times 10^{-6}$ Bq g^{-1}; and Cape Fear in North Carolina, $\sim 29 \times 10^{-6}$ Bq g^{-1}). Along the West Coast, $^{239+240}$Pu activities are low, displaying a geographical distribution similar to what was observed for ^{241}Am with a maximum located in Northern California and high spikes at other locations of the Californian Coast. In particular, like for ^{241}Am, the bivalves collected near Santa Cruz Island–Fraser Point (CA) display the highest $^{239+240}$Pu activity ($\sim 27 \times 10^{-6}$ Bq g^{-1}) on the Pacific Coast.

^{238}Pu concentrations (Tables 2 and 3) are generally low on all three coasts (median of all the values is $\sim 3 \times 10^{-6}$ Bq g^{-1}) and no statistically significant difference is detected among the means for these coasts. However, six locations (Jamaica Bay, NY; Savannah Estuary, GA; Biscayne Bay, FL; Cedar Key, FL; Humboldt Bay, CA; and Whidbey Island, WA) show relatively high concentrations (from ~ 8.6 up to $\sim 59 \times 10^{-6}$ Bq g^{-1}).

Because analysis after radiochemical separation (see the Appendix) achieves a lower detection limit, only β counting results are displayed for ^{137}Cs (Tables 2 and 3). In this case, the values obtained for medians and averages calculated using the complete data set were very similar (~ 190 and $\sim 200 \times 10^{-6}$ Bq g^{-1}, respectively). On the West Coast, higher concentrations (up to 400×10^{-6} Bq g^{-1} at Oceanside, CA) are frequently observed resulting in higher median and average values. The use of the Kruskal–Wallis test reveals that the West Coast activities are significantly different from those of the other coasts ($p < 0.05$).

About 70% of the values reported for ^{90}Sr are below 100×10^{-6} Bq g^{-1} (Tables 2 and 3). Along the West

TABLE 3

Distribution of averages and medians of the radionuclide activities ($\times 10^{-6}$ Bq g^{-1}, except $\times 10^{-2}$ Bq g^{-1} for ^{40}K).

	^{238}Pu		$^{239+240}$Pu		^{241}Am		^{90}Sr		^{137}Cs		^{40}K	
	Average (SD)	Median	Average (SD)	Median	Average (SD)	Median	Average (SD)	Median	Average (SD)	Median	Average (SD)	Median
Total	6 (11)	3	15 (17)	11	22 (27)	8	180 (360)	51	200 (110)	190	29 (7)	29
East	6 (6)	5	16 (16)	11	6 (3)	7	200 (250)	87	140 (60)	150	30 (9)	30
Gulf	14 (25)	5	24 (36)	8	11 (14)	6	130 (140)	71	64 (40)	83	33 (9)	32
West	3 (3)	2	12 (8)	11	36 (31)	24	170 (470)	50	250 (100)	270	28 (4)	29

Coast, the geographic distribution of the activities exhibits a weaker but similar pattern to what has been observed for ^{241}Am. Only one very high value was obtained, near Crescent City–Point Saint George in California (1994×10^{-6} Bq g^{-1}). Along the East Coast, values above 100×10^{-6} Bq g^{-1} are frequent (86% of the data), reaching 733×10^{-6} Bq g^{-1} near Cape Fear (NC). Along the Gulf Coast, the site located in Matagorda Bay (TX) displays the highest activity measured in this area (377×10^{-6} Bq g^{-1}). For ^{90}Sr, no significant difference was observed among the coasts.

In summary, although the variability is very high, the data suggest that the geographical distribution of the radioisotopes varies from one coast to the other for a few radionuclides. In particular, relative to the other US coasts, the West Coast is characterized by higher activities of ^{241}Am and ^{137}Cs.

In the central part of the West Coast (Fig. 2), elevated activities of ^{241}Am were previously observed in the EPA MWP70s. At that time, it was hypothesized that the enrichment in fallout radionuclides was related to the California current and to the associated upwelling of intermediate waters (Goldberg *et al.*, 1978, 1983; Farrington *et al.*, 1983). In the ocean, americium and cadmium exhibit a surface depletion and an enrichment at intermediate depths (Volchok *et al.*, 1971; Livingston *et al.*, 1984). Upwelling of these intermediate waters to the surface would expose organisms to higher concentrations of certain radionuclides and cadmium than are normally found in areas with no upwelling. In the MWP70s study (Goldberg *et al.*, 1983), and in previous NS&T studies (O'Connor, 1990, 1992), high concentrations of cadmium found in the bivalves collected along the central part of the West Coast could support the upwelling hypothesis formulated for the radionuclides.

Isotopic ratios

Isotopic ratios are often used to trace the origin and fate of isotopes in the environment. In our study as well as in the EPA MSW70s study, due to the very low activities measured in the samples, large uncertainties were reported for some of the radionuclide measurements. Consequently, an even larger uncertainty will be associated with the ratio of these activities. It is, however, interesting to note that similar observations can be derived from the data generated in both the EPA and NOAA studies. For example, in the 1990 study, ^{241}Am to $^{239+240}$Pu ratios (Table 2, Figs 3 and 4) are approximately one order of magnitude lower in samples from the East and Gulf Coasts (medians = 0.38 and 0.28, respectively) than in those from the West Coast (median = 3; maximum = 15). Using the Kruskal–Wallis test, the differences between the West Coast median and each of the other coasts (East and the Gulf Coasts) medians are significant at the 0.05 confidence level. Previously, in the EPA MSW70s programme (Goldberg *et al.*, 1978, 1983; Farrington *et al.*, 1983), a similar difference between the West Coast (median = 1.70; maximum = 6.10 and the East and Gulf coasts (median = 0.45 and 0.40, respectively) was observed. These high Pacific ratios could result from a different fractionation of the two nuclides in the marine environment (Noshkin & Bowen, 1975). Livingston & Bowen (1976) have observed that ^{241}Am sinks faster in the ocean than $^{239+240}$Pu, and that the ^{241}Am/$^{239+240}$Pu ratio generally increases in deeper waters and sediments. In the 1970s, the high ratios observed along the Pacific Coast were explained by the upwelling of intermediate Pacific waters. Accumulation of ^{241}Am from the decay of its parent isotope ^{241}Pu ($T_{1/2} = 14.9$ years), is also adding ^{241}Am to the environment. However, this process should not yield ^{241}Am/$^{239+240}$Pu ratios greater than 0.32 before the year 2000 (Livingston *et al.*, 1975, 1984; Livingston & Bowen, 1976). Very low ratios of ^{241}Am/$^{239+240}$Pu exist at a few sites along the East and Gulf coasts. For example (Table 2, Figs 3 and 4), in Massachusetts (near Stover Point and near Deer Island), the ratio is about 0.10 and in Chesapeake Bay (near Calvert Cliff) the ratio is only 0.06. As mentioned above, these differences could merely be due to the large variance in the measurement of the nuclides. However, it is interesting to note that in the EPA MWP70s study, low ratios were found in the same locations, Massachusetts and Chesapeake Bay. In particular, the low ratios observed in both the NOAA and the EPA studies in Massachusetts were associated with high concentrations in the plutonium isotopes. In the 1970s, it was hypothesized that, in this case, the bivalves could have been affected by a fresh input of long-lived plutonium coming from the effluents of a near-by nuclear reactor (Goldberg *et al.*, 1978).

Finally, differences in the isotopic ratios are observable when comparing the different bivalve species (Fig. 4). For example, along the East Coast, ^{241}Am/$^{239+240}$Pu, ^{238}Pu/$^{239+240}$Pu, $^{239+240}$Pu/^{137}Cs, ^{90}Sr/^{137}Cs, and ^{90}Sr/^{40}K ratios are generally lower in mussels (*M. edulis*) than in oysters (*C. virginica*). However, the only statistically significant difference is observed for the $^{239+240}$Pu/^{90}Sr ratio that are lower in oysters than in mussels. This difference may be explained by differences in habitat and/or by differences in bioaccumulation of the various isotopes by the two species. The fact that mussels generally live along the Northeast Coast, attached to hard siliceous substate, off the sea bottom sediments, whereas oysters live mostly along the Southeast Coast, directly on the bottom where they are exposed to a larger load of particles often rich in carbonates, may explain the differences observed between the two species. Differences are also observed between the two species of mussels living along the West Coast. For example, ^{241}Am/$^{239+240}$Pu, $^{239+240}$Pu/^{137}Cs, ^{90}Sr/^{137}Cs, and ^{90}Sr/^{40}K ratios are generally lower in *M. edulis* than in *M. californianus*, but this difference is significant only for the ^{241}Am/$^{239+240}$Pu ratios. Here too, the difference between the two species could be attributed to either a difference in bioaccumulation capability of the two species or to a difference in the marine habitat (high-energy environments located along open coast and in areas exposed to upwellings, for *M. californianus* vs more protected areas for *M. edulis*).

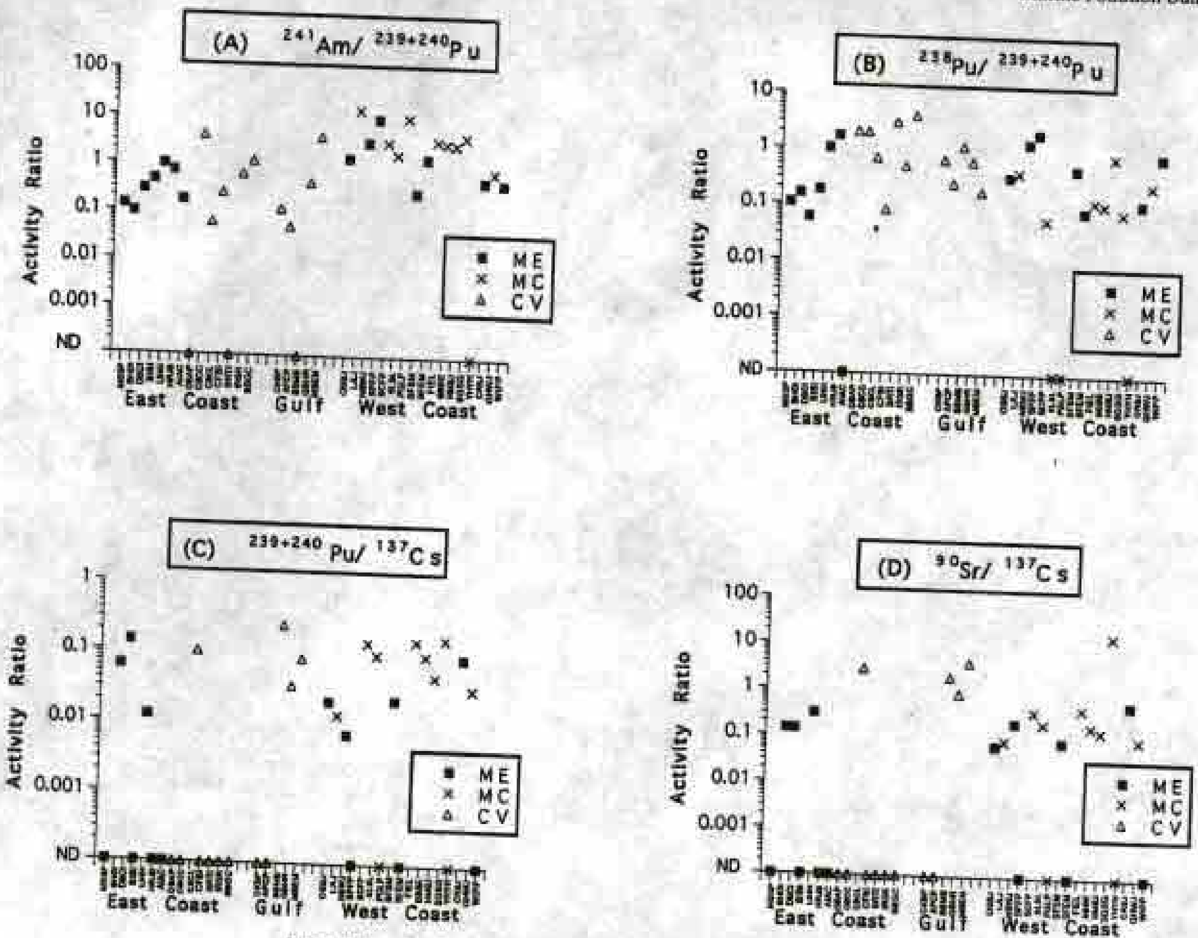

Fig. 3 Plots showing the isotope activity ratios (vertical axes, log scale) obtained for the NOAA NS&T Program displayed in a geographical order (horizontal axes) from the north of the East Coast through the Gulf of Mexico and ending in the Pacific Northwest. The correspondence between site names and acronyms is given in Table 1. The various symbols represent the different species of mollusc used in the study: ME = *Mytilus edulis*; MC = *Mytilus californianus*; CV = *Crassostrea virginica*. A, ^{241}Am/$^{239+240}$Pu ratio; B, ^{238}Pu/$^{239+240}$Pu ratio; C, $^{239+240}$Pu/^{137}Cs ratio; D, ^{90}Sr/^{137}Cs ratio.

emporal trends in the radioactivity of the coastal USA

The present study not only makes it possible to ocument the status of the radioactive contamination in ıe coastal waters of the US but, by comparing the :sults obtained in this study with the EPA MWP70s :sults, allows also for trend analysis over the last 15 ːars or so. In the absence of major new inputs, the ›ncentrations of most of the isotopes would be :pected to decrease over the years in the near coastal ıvironment as a combined result of: (a) declining put from the stratosphere; (b) burial in shallow :positional sediments; (c) dispersion, dilution, and moval to other more remote environmental sinks such deep ocean water or sediments; and (d) physical cay. The decrease in input of fallout radionuclides s been documented in undisturbed sediment cores, ıere the large peak in concentration of fallout radio-clides associated with the 1950s and early 1960s mb tests declines rapidly in recently deposited ficial sediments (Noshkin & Bowen, 1973, 1975; ›en *et al.*, 1981a,b; Bopp *et al.*, 1982). Consequently, when comparing NOAA and EPA data, lower activities are expected in the 1990 NOAA data.

When comparing two sets of data obtained by two different laboratories at two different times (about 15 years apart), technical differences that obscure the interpretation of the results can be expected. With this in mind, we have compared our results with those of the EPA MWP70s in order to see if there are differences in the concentrations of ^{241}Am, $^{239+240}$Pu, ^{238}Pu, and ^{137}Cs, the only radionuclides that were consistently analysed in both programmes. In general, the MWP70s study consisted of one analysis per year in each of the three consecutive years, 1976, 1977, and 1978 (Goldberg *et al.*, 1978, 1983; Farrington, 1983; Farrington *et al.*, 1983; Palmieri *et al.*, 1984) whereas our data represent one analysis for 1990. Consequently, the two sets of data are not absolutely equivalent. However, by comparing for each site the mean of the EPA MWP70s data with the 1990 NS&T data, we were able to test if the results obtained for the period 1976–1978 are different from those obtained in 1990 (Table 4, Fig. 5).

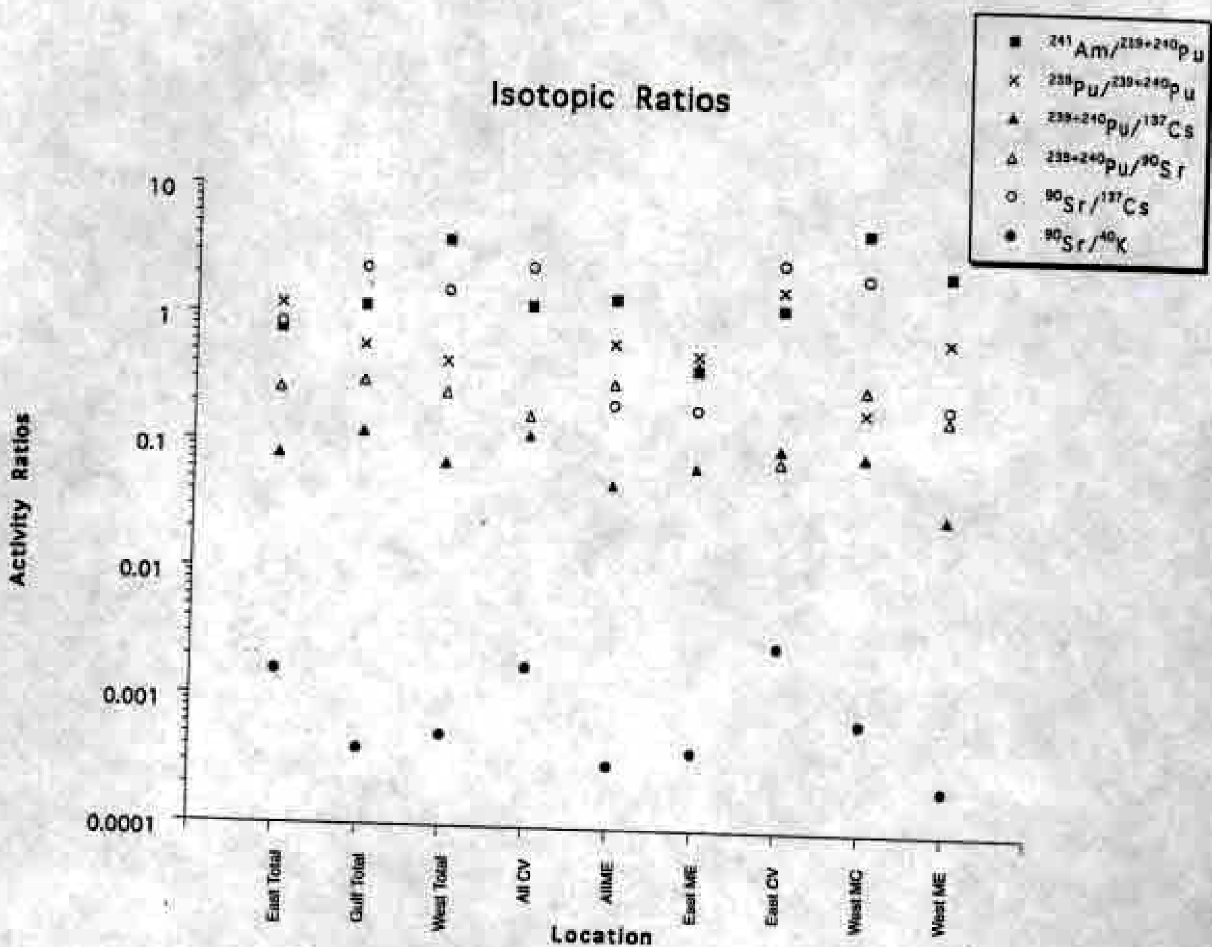

Fig. 4 Plot displaying a summary of the isotope activity ratios (vertical axis, log scale) for the NOAA study. Each point represents the average obtained for each category displayed along the horizontal axis. East Total, average of all the results obtained for the East Coast. Gulf Total, average of all the results obtained for the Gulf Coast. West Total, average of all the results obtained for the West Coast. All CV, average of all the results obtained for *Crassostrea virginica* around the country. All ME, average of all the results obtained for all *Mytilus edulis*. East ME, average of all the results obtained for *Mytilus edulis* along the East Coast. East CV, average of all the results obtained for *Crassostrea virginica* along the East Coast. West MC, average of all the results obtained for *Mytilus californianus* along the West Coast. West ME, average of all the results obtained for *Mytilus edulis* along the West Coast. Different symbols were used for different ratios.

TABLE 4

Comparison of the averages (SD) and medians calculated for NS&T and MWP70s data ($\times 10^{-6}$ Bq g^{-1}).

	^{238}Pu		^{241}Am		$^{239+240}Pu$		^{137}Cs	
	NS&T	EPA*	NS&T	EPA*	NS&T	EPA*	NS&T	EPA*
Average East	6 (6)	1.3 (0.7)	6 (3)	9 (6)	16 (16)	34 (18)	140 (60)	630 (340)
Median	5	1.2	7	7	11	33	150	630
Average Gulf	14 (25)	2.2 (2.2)	11 (14)	4 (2)	24 (36)	25 (22)	64 (40)	550 (900)
Median	5	1.3	6	7	8	32	83	630
Average West	3 (3)	1.3 (0.7)	36 (31)	63 (70)	12 (8)	33 (24)	250 (100)	400 (220)
Median	2	1.1	24	36	11	20	270	470
Average US	6 (11)	1.4 (1.1)	22 (27)	36 (60)	15 (17)	32 (22)	200 (110)	540 (270)
Median	3	1.2	8	13	11	27	190	530

*EPA MWP70s.

Between the mid 1970s and 1990, an increase in ^{238}Pu activity (Fig. 5A) can be observed. The Sign Test indicates that this difference between the two studies is statistically significant ($p < 0.001$). At several sites, the 1990 ^{238}Pu results are almost one order of magnitude greater than the results obtained in the 1970s, suggesting that this isotope may behave in a different manner than expected. Because concentrations reported by both EPA and NOAA are extremely low, very close to the detection limits, the precision of the data is low (the coefficient of variation reaches 300% in some cases for our results and up to 200% for the 1970s study). This ^{238}Pu increase is believed to be an artefact due to differences in the analytical techniques used in the two studies (the early data could be too low or our data could be too high). Although it is impossible to verify the results acquired more than 15 years ago, it will be possible to verify our data by repeating the survey as soon as possible and by using replicate analyses. In the meantime, great prudence must be exercised when interpreting these data and new analyses are necessary to sort out analytical uncertainties from real differences.

For $^{239+240}$Pu, when comparing the averages (Fig. 5C), a significant decrease has been observed ($p < 0.1$).

In 17 cases out of 28, ^{241}Am is lower in the 1990 study than in the mid 1970s study (Table 4, Fig. 5B). The Sign Test, however, shows that this difference is not statistically significant ($p < 0.5$).

In all the cases, radiocesium (^{137}Cs) activities are also significantly lower (Fig. 5D) in 1990 than in the mid-1970s ($p < 0.01$). Between the mid-1970s and 1990, ^{137}Cs activities have decreased by up to a factor of 8 (Table 4), reflecting the very rapid burial and the shorter half-life of ^{137}Cs compared to the other radioisotopes ($T_{1/2} = 30$ years for ^{137}Cs compared with 6580 years for ^{240}Pu, 24 400 years for ^{239}Pu, and 458 years for ^{241}Am).

In summary, except for the ^{238}Pu results, it appears that the radionuclide activities are often lower in 1990

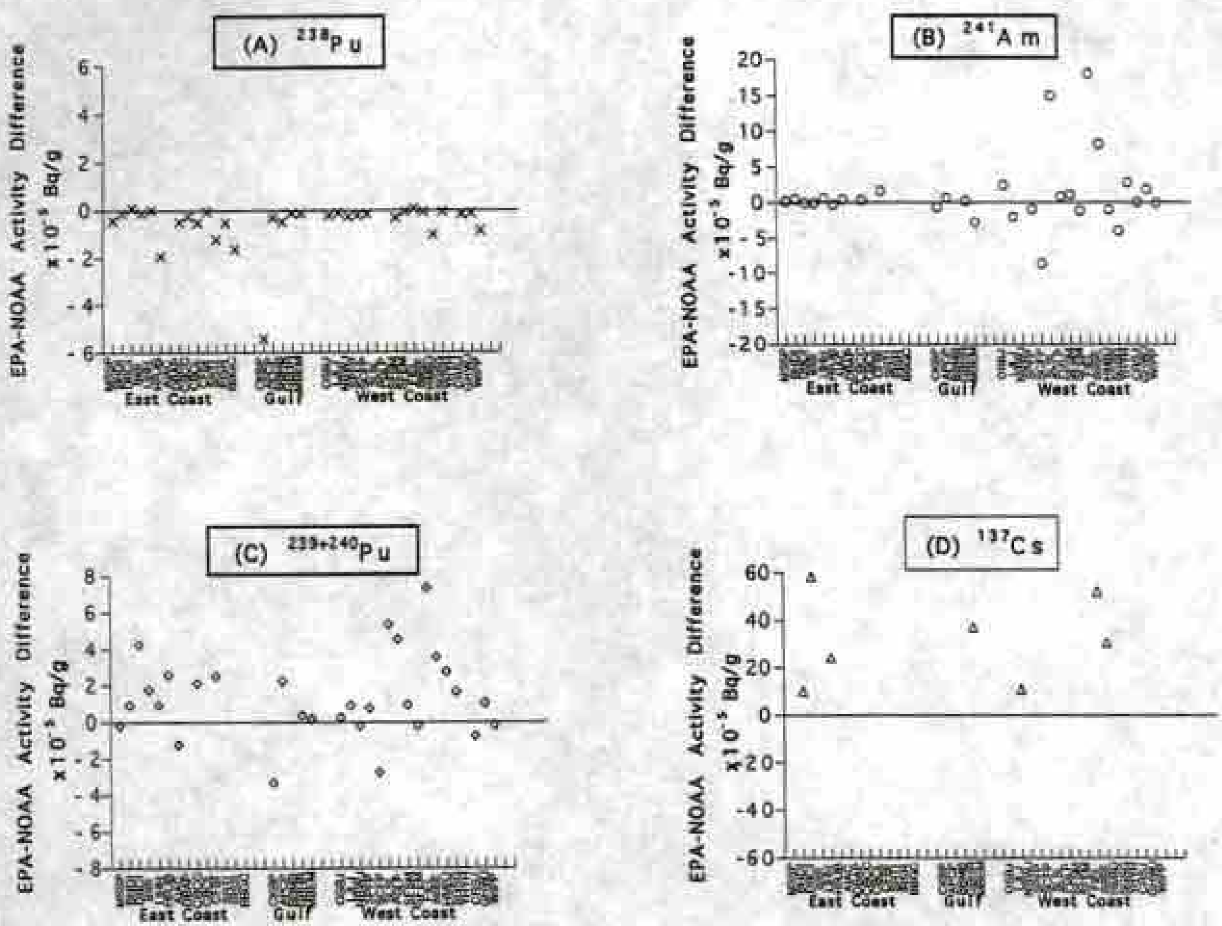

Fig. 5 Plot showing the geographical distribution (horizontal axes) of the difference in activity (vertical axes, Bq g^{-1} × 10^{-5}) of the radioisotopes measured in the MWP70s and in the NOAA NS&T studies. At each site, the results are expressed as the difference between the mean of EPA's activities (1976, 1977, 1978) minus NOAA's activities. The horizontal zero line represents no difference between the two studies. The points lying above the zero line represent sites for which 1970s activity was higher than 1990s activity. Conversely, the points lying under the zero line represent sites for which 1970s activity was lower than 1990s activity. A, comparison for ^{238}Pu; B, comparison for ^{241}Am; C, comparison for $^{239+240}$Pu; D, comparison for ^{137}Cs.

than in the mid-1970s, clearly exhibiting the same decreasing trend observed in most coastal sediments.

Conclusion

The results obtained in this study show that over the last 15 years, $^{239+240}Pu$, and ^{137}Cs concentrations in bivalves have decreased significantly and that in many cases the ^{241}Am activities are also lower in 1990 than in the mid-1970s. These decreases reflect the ban on atmospheric nuclear testing and the decrease of fallout radionuclides in the environment. The new data, like the results obtained for the period 1976–1978, show that ^{241}Am activities are higher in samples collected along the West Coast than in bivalves sampled at other locations. Previous studies have related this observation to the upwelling of intermediate Pacific waters associated with the California Current. In this study, a few spikes of activation products were detected in the vicinity of nuclear power plants. In general, the radionuclide activities measured at the 36 sites studied along the coasts of the US are low.

Differences in the radionuclide activity of bivalves collected in the coastal US can be explained by differences in fractionation among radionuclides in the marine environment, by ingrowth of ^{241}Am from ^{241}Pu decay, by local input of radioisotopes associated with nuclear power plants, and by exposure/bioaccumulation differences observed not only between oysters and mussels, but also between various species of mussels.

The authors are grateful to the NOAA Oxford Laboratory, the Maryland Department of Natural Resources, Battelle, and Texas A&M University for their assistance in collecting and preparing the bivalves used in this study. Many thanks to Douglas Wolfe (NOAA) for providing invaluable information on the environmental behaviour of radionuclides and for criticizing this manuscript in a very constructive way. The authors gratutide is expressed to Andrew Robertson (NOAA) for the numerous reviews of this manuscript and for his helpful comments. Finally, the authors want also to thank Thomas O'Connor (NOAA) for reviewing this manuscript and Jeffrey Fritsen (Versar) for providing reference documentation.

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Appendix: Analytical Method (after TMA/NORCAL 1991–1992)

Once mollusc soft tissues were received by the analytical laboratory, the samples were redried, reweighed, classed, and ashed at 425°C. After the ashing step was completed, the entire sample was placed into either a 100 ml jar or a 15 ml petri dish for γ counting. The geometries were double-checked to verify accurate and current calibrations. Counting was performed with high-resolution, low-background γ spectrometers. High-purity germanium (HPGe) detectors were used to analyse for ^{7}Be, ^{40}K, ^{58}Co, ^{60}Co, ^{65}Zn, ^{110}Ag, and ^{137}Cs. The typical background for ^{60}Co was about 0.08 count per minute (cpm) and for ^{137}Cs, the typical background was about 0.07 cpm. A standard nuclear data peak search routine (ND6620) was used to identify γ emissions, and calculations were done using a TMA/Norcal program, which was double-checked by the staff. This included: verifying data inputs (e.g. aliquot, reference time, geometry, etc.), reviewing the automated peak search routine, verifying peak subtraction, and double-checking the peak library to verify that all the isotopes present in the sample were accounted for.

After γ counting, the ashed material was dissolved and ^{241}Am, $^{239+240}$Pu, ^{238}Pu, ^{137}Cs, and ^{90}Sr were chemically separated. Techniques used to quantify the radionuclides of interest are discussed in Wessman *et al.* (1971, 1977, 1978). Because of the high sensitivity needed for the analysis, sequential determination was performed. A brief discussion of the methods used for chemical separations and counting follows (after TMA/Norcal, 1991, 1992).

After an initial leaching with nitric acid (HNO_3) and hydrogen peroxide, the samples were filtered and the filters were ashed and dissolved using a mixture of concentrated hydrofluoric acid (HF)+HNO_3+hydrochloric acid (HCl). All dissolution fractions were combined, dried, and dissolved in 8 M HNO_3.

Aliquots (80% of the total solution) were taken, ^{242}Pu and ^{243}Am tracers and a yttrium carrier were added, and the solutions were equilibrated and the volume of the 8 M HNO_3 solution reduced.

Plutonium was initially extracted from the sample in a nitric acid solution on a large-scale AG 1×8 anion resin column and eluted with HNO_3+HF. The eluant was then further purified on a second small scale nitrate column of AG 1×8 anion resin. The purified fraction was electro-deposited onto a 1 in. stainless-steel disc and submitted for α spectrometry. Each α spectrum was obtained from one of the 26 solid-state 450 mm^2 surface barrier diodes used by TMA/Norcal. Each detector utilizes 256 channels in a Nuclear Data ND66 computer controlled multichannel analyser system. The sample was counted for at least 1000 min with the spectra collected in 256 channels over the 3.6–7.00 MeV energy region. Energy calibration sources were counted before and after the sample to set peak integration limits. A background measurement and evaluation programme was maintained for each detector, with background d... within the regions integrated for the spectrometric analysis. The efficiencies varied from 24 to 33%.

Strontium-90 was analysed by isolating the ^{90}Y daughter product ($T_{1/2}$=64 h) and β counting up to five times over a period of 2 weeks. A least squares regression was used to calculate ^{90}Y at separation and equilibrium was assumed in the calculation of ^{90}Sr activity. Chemical purification was performed using DDCP (*n,n*-diethyl dicarbamoyl phosphonate) extraction out of the column load fraction from the initial Pu column. The yttrium was back-extracted into dilute HNO_3. Hydroxide, fluoride and oxalate precipitations were performed for further purification. A mixed nitric acid+alcohol anion column was run to separate the Am species which had been carried with the yttrium to this point. Further precipitations were performed and the purified yttrium fraction was mounted on a planchet as an yttrium oxide (Y_2O_3), weighed for chemical recovery, and β counted on a gas flow proportional detection system. The yttrium planchets mounted for ^{90}Sr analysis had default counting instructions for a 200 min first count. In actuality, the great majority had a 400 min first count. This first count was used in determining the detection limit. Counts of 100–200 min were repeated until the count rate dropped below 0.2 counts per minute (cpm) or the count rate became indistinguishable from the background. The interval of counting varied from 1 to 3 days. Most samples received only two or three total β counts since their activities were low. The β counting is described further under the cesium section.

Because the γ counting of the samples for ^{137}Cs generally gave values close to or below detection limits, ^{137}Cs was analysed by β counting after radiochemical purification in the 19 samples for which there was enough material left. In these cases, the remaining sample aliquot (20% of the original sample) was taken, cesium carrier added, and the solution adjusted to a pH of 1.0. The cesium fraction was carried on ammonium molybdophosphate crystals, dissolved in a basic EDTA solution, and run through a Biorex-40 cation exchange column. The dilute HCl eluant was concentrated and further purified by precipitation of cesium silicotungstate and, finally, cesium chloroplatinate. This precipitate was mounted, weighed for recovery, and submitted for β counting. Each ^{137}Cs measurement was performed on one of the 14 low background Geiger detectors on-line. The backgrounds were approximately 0.5 cpm and the data from each detector were corrected for individual differences in detector sensitivity. The system was directly connected to the PDP 11/84 computer for data acquisition and transfer. The nominal efficiency for ^{137}Cs, including self-absorption effects for precipitate thickness, was approximately 35%.

A very strict quality assurance programme (QAP) was applied during these analyses. In particular all the chemical separations were performed in a 'low level laboratory', which is restricted to samples with activity ranging from zero to a few Becquerels (Bq). In addition, environmental and 'zero level' samples were treated in dedicated modules inside the low level laboratory reserved for this area. In particular, brand-new glassware and Teflon containers were used for this project. Cross contamination was prevented by segregating the samples by activity level upon their arrival in the laboratory.

'Laboratory Intercomparison Studies Program' for various matrices, including α, β, and γ emitter isotopes, were routinely performed. Standards from the National Institute of Standards and Technology (NIST), the United Kingdom Atomic Energy Authority (UKAEA), and others were processed on a routine basis. Finally, TMA/Norcal had participated in several collaborative programmes of procedure testing and standardization of reference material.